March 16, 2005

SOP 5

Recommended Standard Operations Procedure for Using a 3-1 Weighing Design

1. Introduction

1.1. Purpose

The 3-1 weighing design is a combination of three double substitution comparisons of three weights of equal nominal value; a standard, an unknown weight, and a second standard called a check standard. (The check standard may be made up of a summation of weights.) The weights are compared using an equal-arm, single-pan mechanical, full electronic, or a combination balance utilizing built-in weights and a digital indication. The specific SOP for the double substitution procedure for each balance is to be followed. The 3-1 weighing design provides two methods of checking the validity of the measurement using an F-test to check the measurement process and a t-test to evaluate the stability of the standard and check standard. Hence, the procedure is especially useful for high accuracy calibrations in which it is critical to assure that the measurements are valid and well documented. This procedure is recommended as a minimum for precision calibration of laboratory working standards that are subsequently used for lower level calibrations and for routine calibration of precision mass standards used for balance calibration. For surveillance of reference and working mass standards and calibration of precision mass standards used to calibrate other mass standards, see SOP 28 for the use of higher level weighing designs.

1.2 Prerequisites

1.2.1 Calibrated mass standards, traceable to NIST, with valid calibration certificates must be available with sufficiently small standard uncertainties for the intended level of calibration. Reference standards should only be used to calibrate the next lower level of working standards in the laboratory and should not be used to routinely calibrate customer standards.

1.2.2 The balance used must be in good operating condition with sufficiently small process standard deviation as verified by F-test values, pooled short term standard deviations, and by a valid control chart for check standards or preliminary experiments to ascertain its performance quality when new balances are put into service.

1.2.3 The operator must be experienced in precision weighing techniques. The operator must have specific training in SOP 2, SOP 4, SOP 5, SOP 29, and be familiar with the concepts in GMP 10.

1.2.4 The laboratory facilities must meet the following minimum conditions to meet the expected uncertainty possible with this procedure:

Table 1. Environmental conditions

Echelon	Temperature	Relative Humidity (percent)
I	20 °C to 23 °C, allowable variation of ± 1 °C Maximum change of 0.5 °C/h	40 to 60 ± 5
II	20 °C to 23 °C, allowable variation of ± 2 °C Maximum change of 1.0 °C/h	40 to 60 ± 10

2 Methodology

2.1 Scope, Precision, Accuracy

This method can be performed on any type of balance using the appropriate double substitution SOP for the particular balance. Because considerable effort is involved, this weighing design is most useful for calibrations of the highest accuracy. The weighing design utilizes three double substitutions to calibrate a single unknown weight. This introduces redundancy into the measurement process and permits two checks on the validity of the measurement; one on accuracy and stability of the standard and the other on process repeatability. A least-squares best fit analysis is done on the measurements to assign a value to the unknown weight. The standard deviation of the process depends upon the resolution of the balance and the care exercised to make the required weighings. The accuracy will depend upon the accuracy and uncertainty of the calibration of the standard weights and the precision of the comparison.

2.2 Summary

A standard weight, S, an unknown weight, X, and a check standard, S_c are intercompared in a specific order using the double substitution procedure. The balance and the weights must be prepared according to the appropriate double substitution SOP for the particular balance being used. Once the balance and weights have been prepared, all readings must be taken from the reading scale of the balance without adjusting the balance or weights in any way. Within a double substitution all weighings are made at regularly spaced time intervals to average out any effects due to instrument drift. Because of the amount of effort required to perform the 3-1 weighing design, the procedure includes the air buoyancy correction.

2.3 Apparatus/Equipment Required

2.3.1 Precision analytical balance or mass comparator with sufficient capacity and resolution for the calibrations planned.

2.3.2 Working standard weights and sensitivity weights with valid calibrations traceable to NIST.

2.3.3 Small working standards with valid calibrations traceable to NIST to be used as tare weights.

2.3.4 Uncalibrated weights to be used to adjust the balance to the desired reading range or adequate optical or electronic range for the intended load and range.

2.3.5 Forceps to handle the weights or gloves to be worn if the weights are moved by hand.

2.3.6 Stop watch or other timing device to observe the time of each measurement or the operator is experienced with determining a stable indication. If an electronic balance is used that has a means for indicating a stable reading, the operator may continue to time readings to ensure consistent timing that can minimize errors due to linear drift.

2.3.7 Thermometer accurate to 0.10 °C to determine air temperature.[1]

2.3.8 Barometer accurate to 0.5 mm of mercury (66.5 Pa) to determine air pressure.

2.3.9 Hygrometer accurate to 10 percent to determine relative humidity.

2.4 Procedure

2.4.1 Place the test weight and standards in the balance chamber or near the balance overnight to permit the weights and the balance to attain thermal equilibrium. The equilibration time is particularly important with weights larger than 1 gram. Conduct preliminary measurements to determine the tare weights that may be required, the size of the sensitivity weight required, adjust the balance to the appropriate reading range of the balance indications, and to exercise the balance. Refer to the appropriate double substitution SOP

[1]The thermometer, barometer, and hygrometer are used to determine the air density at the time of the measurement. The air density is used to make an air buoyancy correction. The accuracies specified are recommended for high precision calibration. Less accurate equipment can be used with only a small degradation in the overall accuracy of the measurement (See SOP 2).

for details.

2.4.2 Weighing Design Matrix

The following table shows the intercomparisons to be made in the 3-1 design, in a matrix format as shown in NBS Technical Note 952, Designs for the Calibration of Standards of Mass, J. M. Cameron, M. C. Croarkin, and R. C. Raybold, 1977.:

Weight ID Comparison	S	X	Sc
a_1	+	-	
a_2	+		-
a_3		+	-
Standard	+		
Check Standard			+

This design is represented as design ID “A.1.1”in Technical Note 952, with the exception that the design order is reversed and Restraint B is used. The restraint is another name for the “standard” used in the comparison that may be found in NBS Technical Note 952. This matrix may be useful for anyone using the NIST Mass Code for data reduction. When creating a data file for this design, the design matrix will appear as follows:

restraint	1	0	0
Check	0	0	1
following series sum	0	0	0
Report	0	1	1
1st double sub	1	-1	0
2nd double sub	1	0	-1
3rd double sub	0	1	-1

2.4.3 Measurement Procedure

Record the pertinent information for the standard, S, unknown, X, and check standard, S_c, as indicated on a suitable data sheet such as the one in the Appendix of this SOP. Record the laboratory ambient temperature, barometric pressure, and relative humidity. Perform the measurements in the order shown in the following table.

Double Substitution	Measurement Number	Weights on Pan	Observation
a_1: S vs X	1	$S + t_s$	O_1
	2	$X + t_x$	O_2
	3	$X + t_x + sw$	O_3
	4	$S + t_s + sw$	O_4
a_2: S vs S_c	5	$S + t_s$	O_5
	6	$S_c + t_{sc}$	O_6
	7	$S_c + t_{sc} + sw$	O_7
	8	$S + t_s + sw$	O_8
a_3: X vs S_c	9	$X + t_x$	O_9
	10	$S_c + t_{sc}$	O_{10}
	11	$S_c + t_{sc} + sw$	O_{11}
	12	$X + t_x + sw$	O_{12}

where:

Variable	Description
t_s	calibrated tare weights carried with S
t_x	calibrated tare weights carried with X
t_{sc}	calibrated tare weights carried with S_c
sw	calibrated sensitivity weight

3 Calculations

3.1 Calculate the air density, ρ_A, as described in the Appendix to SOP No. 2.

3.2 Calculate the measured differences, a_1, a_2, and a_3, for the weights used in each double substitution using the following formula (note: do not confuse this formula with the calculations used in SOP 4; the signs will be opposite from Option A of SOP 4):

$$a_x = \frac{(O_1 - O_2 + O_4 - O_3)}{2} \frac{M_{sw}\left(1 - \frac{\rho_A}{\rho_{sw}}\right)}{O_3 - O_2}$$

where:

Variable	Description
M_{sw}	mass of the sensitivity weight
ρ_{sw}	density of the sensitivity weight

3.3 Calculate the short term within process standard deviation, s_w, for the 3-1 weighing design. This standard deviation has one degree of freedom.

$s_w = 0.577(a_1 - a_2 + a_3)$

3.4 Compute the F statistic which compares the short term within process standard deviation, s_w, to the pooled within process standard deviation. (See chapter 8.4 and 8.5 for a discussion of the statistics used in weighing designs.)

$$F\text{ - }statistic = \frac{s_w^{\,2}}{(\,Pooled\ s_w\,)^2}$$

The F-statistic so computed must be less than the F-value obtained from an F-table at 99 % confidence level (Table 9.5) to be acceptable. The F-value is obtained from the F-table for numerator degrees of freedom equal one, and denominator degrees of freedom equal to the number of degrees of freedom in the pooled within process standard deviation. If the data fails the F-test and the source of the error cannot be determined conclusively, the measurement must be repeated.

3.5 Compute the observed mass value of the check standard.

Compute the least-squares measured difference d_{sc} for S_c.

$$d_{s_c} = \frac{-a_1 - 2a_2 - a_3}{3}$$

3.6 Compute the observed mass of S_c, M_{sc}.

$$M_{sc} = \frac{M_s\left(1 - \frac{\rho_A}{\rho_s}\right) + d_{sc} + M_{t_s}\left(1 - \frac{\rho_A}{\rho_{t_s}}\right) - M_{t_{sc}}\left(1 - \frac{\rho_A}{\rho_{t_{sc}}}\right)}{\left(1 - \frac{\rho_A}{\rho_{sc}}\right)}$$

3.7 Evaluation of the observed mass of S_c, M_{sc} .

The mass determined for the check standard should be plotted on the control chart and must lie within the control limits. If it does not, and the source of error cannot be found, the measurement must be repeated. The 'Accepted M_{Sc}' is the mean of the historically observed mass values for the check standard.

|Observed M_{Sc} – Accepted M_{Sc}| > 3sd	Status: Out of Control
2sd < |Observed M_{Sc} – Accepted M_{Sc}| < 3sd	Status: In Control*Warning
|Observed M_{Sc} – Accepted M_{Sc}| < 2sd	Status: In Control

Perform an E_{normal} test to compare the mean value of the M_{sc} value from the 3-1 design to a calibration value that has demonstrated measurement traceability for the check standard.

$$E_n = \frac{\left|\overline{M}_{Sc} - CalibratedM_{Sc}\right|}{\sqrt{U^2_{M_{sc}} + U^2_{CalibratedM_{sc}}}}$$

The E_{normal} value must be less than one to pass.

3.8 Compute the least-squares measured difference, d_x, for X.

$$d_x = \frac{-2a_1 - a_2 + a_3}{3}$$

3.9 Compute the mass of X, M_x.

$$M_x = \frac{M_s\left(1 - \frac{\rho_A}{\rho_s}\right) + d_x + M_{t_s}\left(1 - \frac{\rho_A}{\rho_{t_s}}\right) - M_{t_x}\left(1 - \frac{\rho_A}{\rho_{t_x}}\right)}{\left(1 - \frac{\rho_A}{\rho_x}\right)}$$

where:

Variable	Description
ρ_A	air density
M_i	mass for weight I
ρ_i	reference density for weight I

3.10 Calculate the conventional mass of X versus the desired reference density of 8.0 g/cm^3 or apparent mass of brass (8.3909 g/cm^3). It is recommended that the conventional mass versus 8.0 g/cm^3 be reported unless otherwise requested. The density of X, ρ_x, must be entered in g/cm^3. (See SOP No. 2)

3.10.1 Conventional mass

$$CM_x\, vs. 8.0 = \frac{M_x\left(1 - \frac{0.0012}{\rho_x}\right)}{0.999850}$$

3.10.2 Apparent mass versus brass (8.3909 g/cm3 at 20 °C)

$$AM_x\, vs. 8.4 = \frac{M_x\left(1 - \frac{0.0012}{\rho_x}\right)}{\left(1 - \frac{0.0012}{8.3909}\right)}$$

4 Assignment of Uncertainty

The limits of expanded uncertainty, U, include estimates of the standard uncertainty of the mass standards used, u_s, plus the uncertainty of measurement, u_m, at the 95 percent level of confidence. See SOP 29, “Standard Operating Procedures for the Assignment of Uncertainty”, for the complete standard operating procedure for calculating the uncertainty. When the 3-1 weighing design is used in conjunction with the Mass Code for data reduction, see SOP 28, “Recommended Standard Operating Procedure for Using Advanced Weighing Designs”, for detailed instructions on calculating the uncertainty components which are required by the Mass Code program.

4.1 The standard uncertainty for the standard, u_s, is obtained from the calibration report. The combined standard uncertainty, u_c, is used and not the expanded uncertainty, U, therefore the reported uncertainty for the standard will need to be divided by the coverage factor k. Since only one standard is used as the restraint for the 3-1 weighing design, the uncertainty of the check standard is not included in assigning an uncertainty to the unknown mass.

4.2 Standard deviation of the measurement process from control chart performance (See SOP No. 9.)

The value for s_p is obtained from the control chart data for check standards using 3-1 weighing designs. Statistical control must be verified by the measurement of the check standard in the 3-1 design.

4.3 Other standard uncertainties usually included at this calibration level include uncertainties associated with calculation of air density and standard uncertainties associated with the density of the standards used.

5 Report

5.1 Report results as described in SOP No. 1, Preparation of Test/Calibration Reports.

Appendix

3-1 Weighing Design When Tare Weights Are Used
(Densities used to compute air buoyancy correction)
(Air buoyancy correction on the tare weights)

Laboratory data and conditions:

Date		Temperature	
Balance		Pressure	
Load		Relative Humidity	
Pooled within process s.d., s_w=		Calculated Air Density	
Check standard s.d., s_p =			

Mass standard(s) data:

ID	Mass = N + C (g)	Density (g/cm^3)	Unc$_{(k=1)}$ (mg)	ID	Mass = N + C (g)	Density (g/cm^3)	Unc$_{(k=1)}$ (mg)
N_x				t_x			
M_s				t_s			
M_{sc}				t_{sc}			
sw							

N = Nominal, C = Correction, M = *True Mass*

Laboratory observations:

Balance Observations					
S - X = a_1		S - S_c = a_2		X - S_c = a_3	
S + t_s		S + t_s		X + t_x	
X + t_x		S_c + t_{sc}		S_c + t_{sc}	
X + t_x + sw		S_c + t_{sc} + sw		S_c + t_{sc} + sw	
S + t_s + sw		S + t_s + sw		X + t_x + sw	
a_1 =		a_2 =		a_3 =	

Note: dotted line represents decimal point.

Calculate "a" values: $$a_x = \frac{(O_1 - O_2 + O_4 - O_3)}{2} \; \frac{M_{sw}\left(1 - \frac{\rho_A}{\rho_{sw}}\right)}{O_3 - O_2}$$

Calculate short term within process standard deviation and conduct F-test:

$s_w = .577(a_1 - a_2 + a_3)$

$$F\text{ - }statistic = \frac{s_w^2}{(\ Pooled\ s_w\ )^2} < value \quad F\text{ - }table\ 9.5$$

F-test passes? Yes No

Evaluate check standard (by plotting on a control chart or with a t-test):

$$d_{s_c} = \frac{-a_1 - 2a_2 - a_3}{3}$$

$$M_{s_c} = \frac{M_s\left(1 - \frac{\rho_A}{\rho_s}\right) + d_{s_c} + M_{t_s}\left(1 - \frac{\rho_A}{\rho_{t_s}}\right) - M_{t_{sc}}\left(1 - \frac{\rho_A}{\rho_{t_{sc}}}\right)}{1 - \frac{\rho_A}{\rho_{s_c}}}$$

Check standard passes? Yes No

If both F-test and check standard pass the tests, calculate the mass of the unknown test item:

$$d_x = \frac{-2a_1 - a_2 + a_3}{3}$$

$$M_x = \frac{M_s\left(1 - \frac{\rho_A}{\rho_s}\right) + d_x + M_{t_s}\left(1 - \frac{\rho_A}{\rho_{t_s}}\right) - M_{t_x}\left(1 - \frac{\rho_A}{\rho_{t_x}}\right)}{1 - \frac{\rho_A}{\rho_x}}$$

$$CM_x\ vs\ \rho_{ref} = \frac{M_x\left(1 - \frac{0.0012}{\rho_x}\right)}{1 - \frac{0.0012}{8.0}}$$

where ρ_{ref} refers to the reference density.

Example

3-1 Weighing Design When Tare Weights Are Used
(Densities used to compute air buoyancy correction)
(Air buoyancy correction on the tare weights)

Laboratory data and conditions:

Date	8/18/96	Temperature	21.7
Balance	AT 1005	Pressure	753.5
Load	1 kg	Relative Humidity	45
Pooled within process s.d., s_w=	0.023 mg	Calculated Air Density	1.182 mg/cm^3
Check standard s.d., s_p =	0.10 mg		

Mass standard(s) data:

ID	Mass = N + C	Density (g/cm^3)	Unc$_{(k=1)}$ (mg)	ID	Mass = N + C (g)	Density (g/cm^3)	Unc$_{(k=1)}$ (mg)
N_x	1000 g	7.84	TBD	t_x	NA		
M_s	999.99850 g	8	0.0327 mg	t_s	NA		
M_{sc}	1000.0023 g	8	0.0327 mg	t_{sc}	NA		
sw	50.086 mg	8.41	0.0010 mg				

N = Nominal, C = Correction, M = *True Mass*

Laboratory observations:

Balance Observations					
S - X = a_1		S - S_c = a_2		X - S_c = a_3	
S + t_s	10.00	S + t_s	10.30	X + t_x	15.50
X + t_x	15.30	S_c + t_{sc}	14.00	S_c + t_{sc}	14.10
X + t_x + sw	65.30	S_c + t_{sc} + sw	64.10	S_c + t_{sc} + sw	64.00
S + t_s + sw	60.10	S + t_s + sw	60.40	X + t_x + sw	65.60
a_1 = - 5.25829		a_2 = - 3.69845		a_3 = 1.50538	

Note: dotted line represents decimal point.

Calculate “a” values:

$$a = \frac{(O_1 - O_2 + O_4 - O_3)}{2} \frac{M_{sw}\left(1 - \frac{\rho_A}{\rho_{sw}}\right)}{O_3 - O_2}$$

Calculate short term within process standard deviation and conduct F-test:

s_w = .577(a_1 - a_2 + a_3) = -0.03142

$$F\text{ - }statistic = \frac{s_w^{\ 2}}{(Pooled\ s_w)^2} < value \quad F\text{ - }table\ 9.5$$

$$F\text{ - }statistic = \frac{-0.03142^2}{0.023^2} = 1.87 \ < \ 7.31 value \quad F\text{ - }table\ 9.5\ d.f. = 40$$

F-test passes? **<u>Yes</u>** No

Evaluate check standard (by plotting on a control chart or with a t-test):

$$d_{s_c} = \frac{-a_1 - 2a_2 - a_3}{3} = \frac{-5.25829 - 2(-3.69845) - 1.50538}{3} = 3.71660\ mg$$

$$M_{s_c} = \frac{M_s\left(1 - \frac{\rho_A}{\rho_s}\right) + d_{s_c} + M_{t_s}\left(1 - \frac{\rho_A}{\rho_{t_s}}\right) - M_{t_{s_c}}\left(1 - \frac{\rho_A}{\rho_{t_{s_c}}}\right)}{1 - \frac{\rho_A}{\rho_{s_c}}}$$

$$M_{s_c} = \frac{999.9985\ g\left(1 - \frac{0.001182}{8}\right) + 0.00371660}{1 - \frac{0.001182}{8}} = 1000.002217\ g$$

Check standard passes? **<u>Yes</u>** No

If both F-test and check standard pass the tests, calculate the mass of the unknown test item:

$$d_x = \frac{-2a_1 - a_2 + a_3}{3} = \frac{-2(-5.25829) - (-3.69845) + 1.50538}{3} = 5.24014 \ mg$$

$$M_x = \frac{M_s\left(1 - \frac{\rho_A}{\rho_s}\right) + d_x + M_{t_s}\left(1 - \frac{\rho_A}{\rho_{t_s}}\right) - M_{t_x}\left(1 - \frac{\rho_A}{\rho_{t_x}}\right)}{1 - \frac{\rho_A}{\rho_x}}$$

$$M_x = \frac{999.9985 \ g\left(1 - \frac{0.001182}{8}\right) + 0.00524014 \ g}{1 - \frac{0.001182}{7.84}} = 1000.006757 \ g$$

$$CM_x = \frac{M_x\left(1 - \frac{0.0012}{\rho_x}\right)}{1 - \frac{0.0012}{\rho_{ref}}} = \frac{1000.006757 \ g\left(1 - \frac{0.0012}{7.84}\right)}{1 - \frac{0.0012}{8}} = 1000.003695 \ g$$

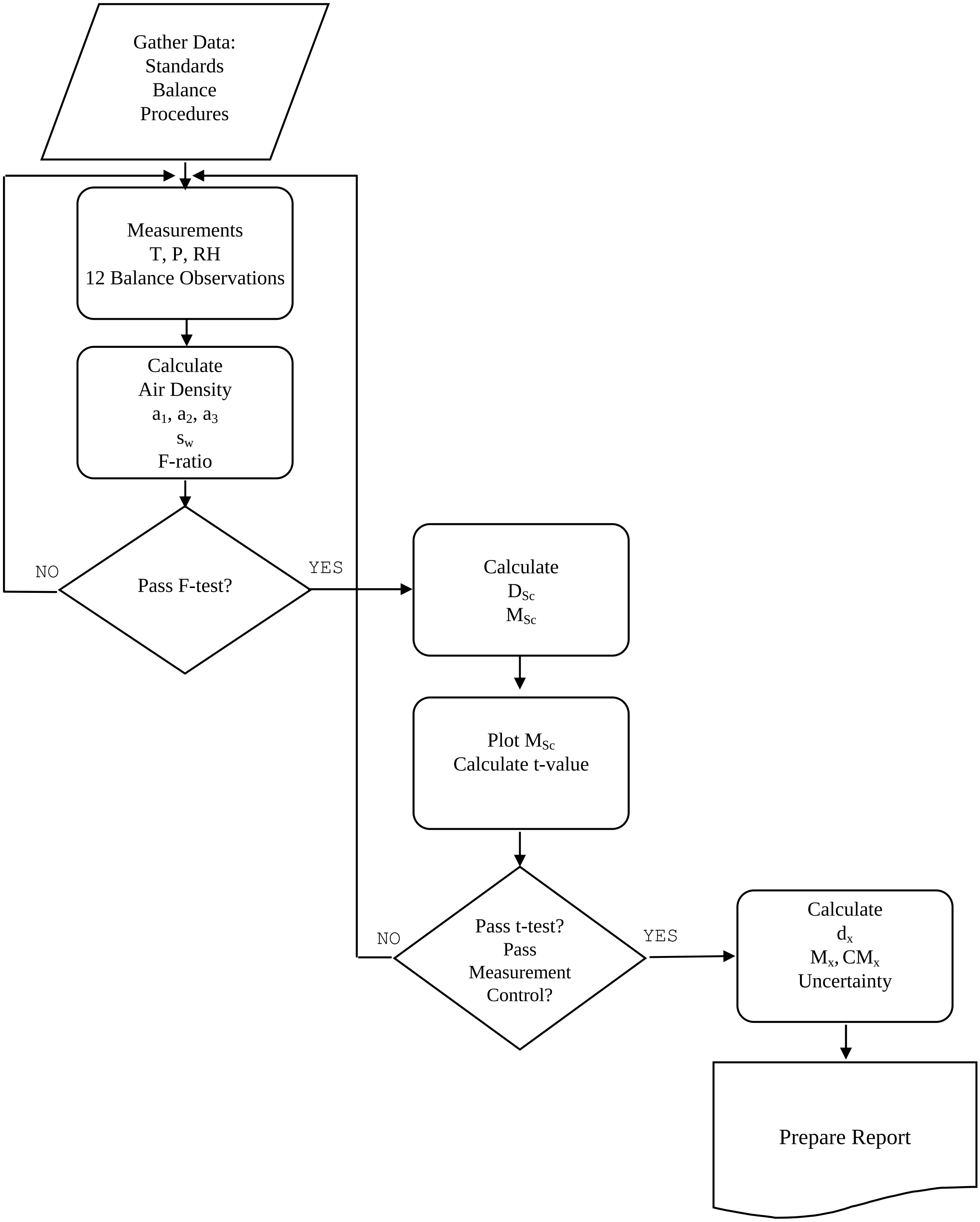
where ρ_{ref} refers to the reference density 8.0 g/cm^3, or conventional mass.

Uncertainty:

$$U = 2 * U_c = 2 * \sqrt{u_s^2 + s_p^2 + u_o^2} = 2 * \sqrt{\left(\frac{0.098 \ mg}{3}\right)^2 + 0.10 \ mg^2 + 0.005 \ mg^2}$$

U = 0.210638 mg = 0.21 mg

C_x = 3.70 mg ± 0.21 mg (Conventional Mass vs 8.0 g/cm^3).



Gather Data:
Standards
Balance
Procedures
Measurements
T, P, RH
12 Balance Observations
Calculate
Air Density
a_1, a_2, a_3
s_w
F-ratio
Pass F-test?
NO
YES
Calculate
D_{Sc}
M_{Sc}
Plot M_{Sc}
Calculate t-value
Pass t-test?
Pass
Measurement
Control?
NO
YES
Calculate
d_x
M_x, CM_x
Uncertainty
Prepare Report